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Technical Report No. 9

PREPARATION AND CHARACTERIZATION OF CHROMIUM(III) OXIDE FILMS

BY A NOVEL SPRAY PYROLYSIS METHOD

by

Y-T. Qian, R. Kershaw, K. Dwight and A. Wold

Prepared for Publication in

MATERIALS RESEARCH BULLETIN

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JAN 23 1991  
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December 21, 1990

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## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT APPROVED FOR PUBLIC RELEASE DISTRIBUTION UNLIMITED	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report #9		5. MONITORING ORGANIZATION REPORT NUMBER(S) NOOG 14-89-J-1849	
6a. NAME OF PERFORMING ORGANIZATION BROWN UNIVERSITY AARON WOLD	6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH CODE 427 113	
6c. ADDRESS (City, State, and ZIP Code) DEPARTMENT OF CHEMISTRY, BOX H BROWN UNIVERSITY, PROVIDENCE RI 02912		7b. ADDRESS (City, State, and ZIP Code) DR. MARK M. ROSS 800 N. Quincy St. Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO
		TASK NO.	WORK UNIT NO
11. TITLE (Include Security Classification) PREPARATION AND CHARACTERIZATION OF CHROMIUM(III) OXIDE FILMS BY A NOVEL SPRAY PYROLYSIS METHOD			
12. PERSONAL AUTHOR(S) Y-T. Qian, R. Kershaw, K. Dwight and A. Wold			
13a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14 DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION <i>Prepared for Publication in Materials Res. Bull.</i>			
17. COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Chromium(III) oxide films of 2000 Å thickness were deposited on n-type silicon wafers by a novel spray pyrolysis method. Different spray solutions, all containing a chromium acetylacetone complex, gave different rates of film deposition. IR spectroscopy of these films confirmed them to be $\alpha$ -Cr <sub>2</sub> O <sub>3</sub> . The deposited films of $\alpha$ -Cr <sub>2</sub> O <sub>3</sub> were found to be homogeneous and uniform with breakdown potentials in excess of 20 V. The characteristics of films prepared from different spray solutions are compared and discussed.			
(23) <i>* Thin films</i>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

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Accession For	
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Conclusions

Solutions of chromium acetylacetone in acetic acid, in 30% ethanol/water, and in pure ethanol have been evaluated as source materials for the preparation of  $\alpha\text{-Cr}_2\text{O}_3$  films on silicon substrates. These solutions were nebulized, sprayed onto the substrate, and thermally decomposed. The optimum preparative conditions were determined. High quality, uniform films free of pinholes, comprised of small particles, and with high dc breakdown voltages were obtained from all three solutions. Thus, the relatively inexpensive technique of spray pyrolysis is shown to be an effective alternative to evaporation (1), sputtering (1-3), and MOCVD (4) for the preparation of  $\alpha\text{-Cr}_2\text{O}_3$  films. However, there were appreciable differences in deposition rate, in crystallinity, in surface morphology, and in density for films prepared from different solutions.

Acknowledgments

This work was partially supported by the Office of Naval Research, by NSF Contract No. DMR 880 3184, by Eastman Kodak Company and by the GTE Labs, Inc.

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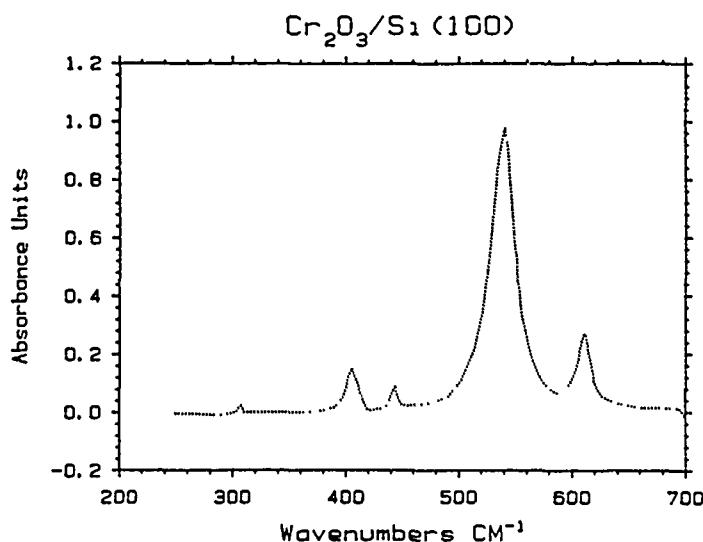


Fig. 3. IR spectra of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> films of 2000 Å thickness.

silicon substrate. Silicon is cubic with  $a=5.43\text{\AA}$ ;  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> is hexagonal with  $a=4.95\text{\AA}$  and  $c=13.58\text{\AA}$ . The (110) plane of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> contains the c axis, and 2 times 13.58 gives 27.16 whereas 5 times 5.43 gives 27.15 for silicon. Thus the c-axis of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> is commensurate with the a-axis of silicon, which may be the reason for its preferential growth.

Films prepared from the 30% ethanol/water<sub>x</sub> solutions produced an unusually intense 006 peak in their x-ray patterns. There do not appear to be any obvious correlations between the (001) plane of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> and the (100) plane of silicon to give rise to preferential growth. However, the typical photomicrograph of similar films (Fig. 2b) shows them to consist of acicular particles. It does not seem unreasonable in this case to attribute the modification of normal  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> x-ray peak intensities to the shape of the particles. Finally, films prepared from pure ethanol solution produce such broad x-ray peaks that the 104 peak at 33.6° and the 110 peak at 36.2° overlap. This confirms the poor crystallinity inferred above from the particle morphology observed by electron microscopy.

Films of approximately 2000Å thickness prepared from all three solutions gave the same IR spectra, shown in Fig. 3. This consists of five distinct absorption peaks which are characteristic of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> (12,13).

DC current-voltage measurements were made on films of approximately 2000Å thickness prepared from all three solutions. No voltage breakdown was observed for potentials up to 20V applied to any of the evaporated gold electrodes. However, films prepared from the 30% ethanol/water solution showed an appreciably greater leakage current (lower resistance) than films prepared from the other solutions. This characteristic may be related to the lower density of these films observed (Fig.2b) by electron microscopy.

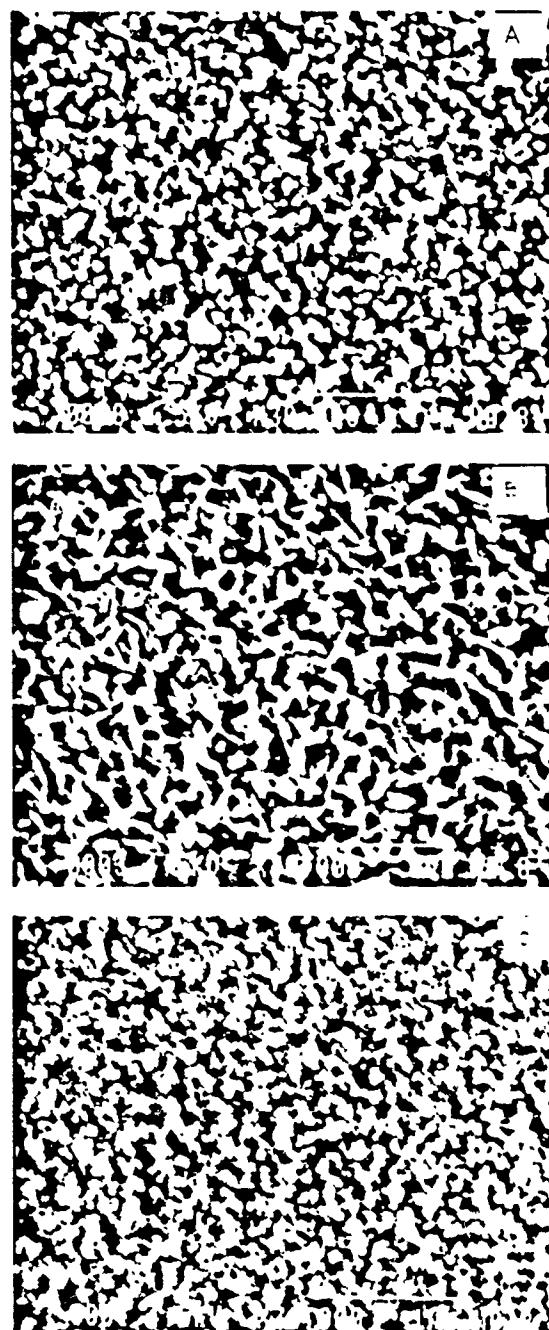
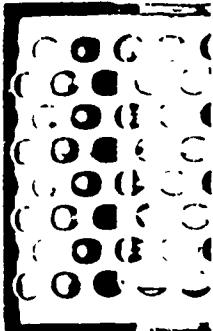


Fig. 2. Electron photomicrographs of  $\alpha\text{-Cr}_2\text{O}_3$  films of 2000 Å thickness prepared from: a) 0.005 M  $\text{Cr}(\text{acac})_3$  in acetic acid; b) 0.007 M  $\text{Cr}(\text{acac})_3$  in 30% ethanol/water; and c) 0.01 M  $\text{Cr}(\text{acac})_3$  in ethanol.



used. The spectra of the films were obtained by subtracting the spectra of the uncoated substrates measured prior to film deposition from the corresponding spectra of the coated substrates measured after deposition.

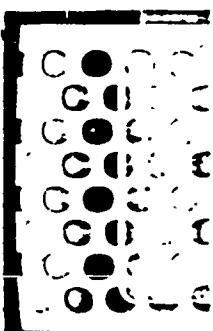
Electrodes for measuring the electrical transport properties of the films were prepared as follows: gold was evaporated through a mask to obtain an array of circular electrodes of area  $1.1 \text{ mm}^2$  each on the surface of the chromium(III) oxide film; an indium alloy (Indalloy #9, Indium Corporation of America) was ultrasonically bonded to the back of the silicon substrate. Contact to a gold electrode was made by touching a gold-tipped micromanipulator to the desired spot. The dc current-voltage behavior was measured with the gold positively biased with respect to the substrate and with the reversed polarity.

#### Results and Discussion

Films of chromium(III) oxide of approximately 2000 Å thickness have been deposited on silicon by the spray pyrolysis of solutions of chromium acetylacetone using the conditions given in Table I. However, the time required for the deposition of this standard thickness varies greatly among the three solutions; 8 hr for the 0.005M solution in acetic acid, 4 hr for the 0.007M solution in 30% ethanol/water, and 2 hr for the 0.01M solution in ethanol. For a given solvent, the deposition time would decrease with increasing concentration of  $\text{Cr}(\text{acac})_3$ . The dramatic observed decrease suggests that the solvent may affect the composition of the complex, and hence its volatility.

The uniformity of the deposited chromium(III) oxide film depends most critically upon the nozzle-to-substrate distance. As shown in Table I, optimum uniformity requires slightly different distances for the three different solutions. The thickness of several films from each solution was measured at different positions with an ellipsometer. For the conditions given in Table I, the thickness of each film was found to be uniform to within 1% except near its very edge. Chromium(III) oxide films of approximately 2000 Å thickness are yellow-green in color - the brightness and uniformity of this color confirmed the uniformity of film thickness.

Photomicrographs of 2000 Å films prepared from the three solutions are shown in Fig. 2. All three films appear to be homogeneous and free of pinholes, but there are some differences. The film prepared from the acetic acid solution is comprised of densely packed small particles (Fig. 2a) of about 400 Å diameter. Their distinct shape indicates appreciable crystallinity. The film prepared from the 30% ethanol/water solution consists of less densely packed, acicular particles (Fig. 2b) of approximately 1000x200 Å. These also show appreciable crystallinity. The films prepared from the pure ethanol solution again consist of densely packed small particles (Fig. 2c) of about 400 Å diameter, but their less distinct shape indicates a less crystalline character.



None of the above 2000 Å films showed any peaks in their x-ray diffraction patterns. Hence films of 4000 Å thickness were similarly prepared. The x-ray diffraction patterns of these thicker films showed only the characteristic peaks of  $\alpha\text{-Cr}_2\text{O}_3$ , which is consistent with the IR results discussed below. However, films prepared from the acetic acid solution produced an unusually strong 110 peak in their x-ray patterns, which indicates that there has been a (110) preferential growth of  $\alpha\text{-Cr}_2\text{O}_3$  on the (100)

reactor by a carrier gas. The nebulized solutions were delivered to the substrate in 5 sec pulses with 15 sec intervals between pulses. The substrates consisted of 1 cm squares of n-type (100) silicon with 8  $\Omega\text{-cm}$  resistivity. They were cleaned and etched immediately prior to the deposition according to the procedure described by Fournier et al.(10). The reactor was heated by a two-zone mirror furnace (Trans-Temp, Chelsea, MA). Typical sets of reaction parameters for obtaining films of 2000 $\text{\AA}$  thickness from the three solutions are given in Table I. Since the carrier gas for the solution of Cr(acac)<sub>3</sub> in pure ethanol was argon (for safety reasons), an additional heating for half an hour at 450 $^{\circ}\text{C}$  in oxygen was necessary.

#### Characterization of films

X-ray diffraction patterns of the films were obtained using a Philips Diffractometer with monochromated high intensity CuK $\alpha_1$  radiation ( $\lambda=1.5404 \text{ \AA}$ ). Diffraction patterns were taken with a scan rate of 1 $^{\circ}$  2 $\theta$ /min over the range 20 $^{\circ} < 2\theta < 70^{\circ}$ .

The thickness of the films was determined by ellipsometry using a Rudolph Research Auto EL-II Ellipsometer. The wavelength of the laser beam was 632.8 nm. The calculation of thickness from the observed data employed the values N<sub>s</sub>=3.877 and K<sub>s</sub>=0.019, respectively, for the real and imaginary parts of the index of refraction of the silicon substrates (11).

The surface morphology of the films was examined by means of a JEOL-840F Scanning Electron Microscope (SEM) operating at 4.5 kV.

The IR spectra were obtained using a Bruker IR 98 FTIR Spectrometer with a deuterated triglycine sulphate detector equipped with a polyethylene window. The light source was a Hg arc; 12, 6, and 3.5  $\mu\text{m}$  mylar beamsplitters were

Table I: Reaction Parameters

Spray Solution:	0.005M in 0.66M Acetic Acid	0.007M in 30% Ethanol/water	0.01M in Ethanol
Substrate Temperature	450 $^{\circ}\text{C}$	450 $^{\circ}\text{C}$	450 $^{\circ}\text{C}$
Carrier Gas	Oxygen	Oxygen	Argon
Flow Rate	3.5L/min	3.5L/min	3.5L/min
Nozzle-Substrate Distance	7.3 cm	7.5 cm	8.5 cm
Cycle Time	20 sec	20 sec	20 sec
Nebulization Time	5 sec	5 sec	5 sec
Number of Cycles	1400	600	300

It was the purpose of this work to investigate the preparation and properties of thin  $\alpha\text{-Cr}_2\text{O}_3$  films deposited on silicon substrates by this spray pyrolysis method. Various solutions of chromium acetylacetone were ultrasonically nebulized, sprayed onto silicon substrates, and thermally decomposed at a low temperature. The resulting chromium(III) oxide films were characterized by x-ray diffraction, ellipsometry, scanning electron microscopy, IR spectroscopy, and their electrical transport behavior.

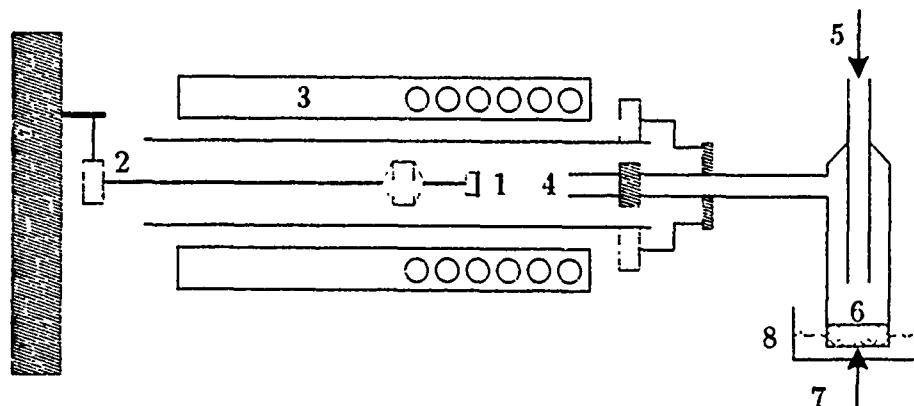
#### Experimental

##### Preparation of solutions

Chromium acetylacetone  $\text{Cr}(\text{acac})_3$  was prepared as described in the literature (9). Three different chromium acetylacetone solutions were used for spray pyrolysis in this investigation: (a) Solutions of 0.005M  $\text{Cr}(\text{acac})_3$  in 0.66M acetic acid were prepared by slowly dissolving 0.438g of  $\text{Cr}(\text{acac})_3$  in 10 ml of acetic acid in a 250ml volumetric flask which was then filled to volume with distilled water; (b) solutions of 0.007M  $\text{Cr}(\text{acac})_3$  in a 30% ethanol/water mixture were prepared by slowly dissolving 0.613g of  $\text{Cr}(\text{acac})_3$  in 75ml of ethanol in a 250ml volumetric flask which was then filled to volume with distilled water; (c) solutions of 0.01M  $\text{Cr}(\text{acac})_3$  in pure ethanol were prepared by putting 0.875g of  $\text{Cr}(\text{acac})_3$  in a 250ml volumetric flask which was then filled to volume with ethanol.

##### Preparation of films

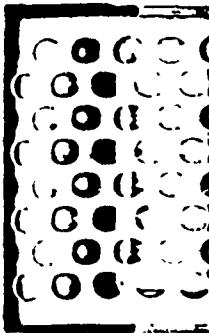
The above solutions of chromium acetylacetone were ultrasonically nebulized, sprayed onto silicon substrates, and thermally decomposed at 450° in the reactor shown in Fig. 1. The solutions were nebulized by a commercial ultrasonic humidifier (Holmes Air) and the resulting mist was swept into the



1 Substrate	5 Carrier gas
2 Substrate rotation motor	6 Solution
3 Furnace	7 Membrane
4 Spray nozzle	8 Ultrasonic Humidifier

Fig. 1. Spray pyrolysis reactor

Mat. Res. Bull., Vol. 25, pp. 1243-1250, 1990. Printed in the USA.  
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## PREPARATION AND CHARACTERIZATION OF CHROMIUM(III) OXIDE FILMS BY A NOVEL SPRAY PYROLYSIS METHOD

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(Received August 2, 1990; Refereed)

### ABSTRACT

Chromium (III) oxide films of 2000 Å thickness were deposited on n-type silicon wafers by a novel spray pyrolysis method. Different spray solutions, all containing a chromium acetylacetone complex, gave different rates of film deposition. IR spectroscopy of these films confirmed them to be  $\alpha\text{-Cr}_2\text{O}_3$ . The deposited films of  $\alpha\text{-Cr}_2\text{O}_3$  were found to be homogeneous and uniform with breakdown potentials in excess of 20 V. The characteristics of films prepared from different spray solutions are compared and discussed.

MATERIALS INDEX: chromium, oxides, thin films



### Introduction

Chromium(III) oxide  $\alpha\text{-Cr}_2\text{O}_3$  is a good candidate for thin insulating layers in electronic devices (1). Such films would be useful for numerous applications as protective coatings (2), as well as for isolation masks on the alumina output windows of high-power klystron tubes (3) to prevent damage arising from the high yield of secondary electrons by alumina.

Previous efforts to prepare films of  $\alpha\text{-Cr}_2\text{O}_3$  on various substrates have used evaporation (1), sputtering (1,2), magnetron sputtering of metallic chromium followed by oxidation (3), and MOCVD (4). Other low temperature methods for the preparation of films of  $\alpha\text{-Cr}_2\text{O}_3$  need to be investigated. Among the alternative methods, spray pyrolysis processing has been shown to be relatively inexpensive and effective for the preparation of oxide films (5). A novel spray pyrolysis process has recently been developed for the preparation of thin oxide films of high quality (6-8).